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March 18, 2005

Journal of Radioanalytical and Nuclear Chemistry

Disclaimer

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January 2005

To be submitted

Journal of Radioanalytical and Nuclear Chemistry

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Second interlaboratory comparison study for the analysis of ^{239}Pu in synthetic urine at the μBq (~100 aCi) level by mass spectrometry

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As a follow up to the initial 1998 intercomparison study, a second study was initiated in 2001 as part of the ongoing evaluation of the capabilities of various ultra-sensitive methods to analyze ^{239}Pu in urine samples. The initial study[1] was sponsored by the Department of Energy, Office of International Health Programs to evaluate and validate new technologies that may supersede the existing fission tract analysis (FTA) method for the analysis of ^{239}Pu in urine at the μBq/l level. The ultra-sensitive techniques evaluated in the second study included accelerator mass spectrometry (AMS) by LLNL, thermal ionization mass spectrometry (TIMS) by LANL and FTA by the University of Utah. Only the results for the mass spectrometric methods will be presented. For the second study, the testing levels were approximately 4, 9, 29 and 56 μBq of ^{239}Pu per liter of synthetic urine. Each test sample also contained ^{240}Pu at a ^{240}Pu/^{239}Pu atom ratio of ~0.15 and natural uranium at a concentration of 50 μBq/ml. From the results of the two studies, it can be inferred that the best performance at the μBq level is more laboratory specific than method specific. The second study demonstrated that LANL-TIMS and LLNL-AMS had essentially the same quantification level for both isotopes. Study results for bias and precision and acceptable performance compared to ANSI N13.30 and ANSI N42.22 have been compiled.

Introduction

The initial 1998 intercomparison study,[1] entitled "Intercomparison Study of Inductively Coupled Plasma Mass Spectrometry, Thermal Ionization Mass Spectrometry and Fission Track Analysis of μBq Quantities of 239Pu in Synthetic Urine" was sponsored by the Department of Energy, Office of International Health Programs (EH-63). The purpose of the study was: (1) to independently evaluate the capability of the fission track analysis (FTA) methodology used by the Brookhaven National Laboratory to measure the 239Pu content in urine specimens collected from the Marshall Islanders and (2) to explore the potential capability of other ultra-sensitive methods for the measurement of μBq quantities of ^{239}Pu in urine. The goal of the project was to evaluate the state-of-the-art fission track and mass-spectrometric methods in terms of accuracy and precision for ^{239}Pu in synthetic urine within a concentration range between 4 to 60 μBq/sample. The results of the first study indicated that mass spectrometric techniques, used with chemical isolation of the plutonium from the urine specimen, were capable of detecting μBq quantities of ^{239}Pu with a level of accuracy and precision that matched or exceeded those found for FTA. Details of the study, including experimental design, synopses of analytical methods and a summary of the test results for bias, precision, and detection capabilities (minimum detectable activity – MDA), have been presented at several national and international conferences including the Bioassay, Analytical and Environmental Radiochemistry Conference (1997) and the MARC IV Conference (1998).

In September of 1999, a meeting was held at the Los Alamos National Laboratory (LANL) to discuss the implementation of a second intercomparison study. Interested participants of the first study and some attendees of the NIST sponsored "1999 Workshop on Standards, Intercomparisons and Performance Evaluations for Low-Level and Environmental Radionuclide Mass Spectrometry and Atom Counting" attended the meeting. The meeting ended with a commitment of three laboratories and one support organization to fund the second study. The second study included a few additional testing elements, compared to the first study, to further determine instrument resolution and detection capabilities as well as the robustness of the chemical separation methods used to eliminate any inherent natural uranium that may result in possible interferences with the method of ^{239}Pu detection. These included the addition of ^{240}Pu to the spiked samples at a world-wide fallout ^{240}Pu/^{239}Pu atom ratio of ~0.15 and the inclusion of natural uranium at a level of 0.05 Bq/sample to all samples including the blanks. This level of natural uranium was chosen to be similar with the background urine levels in the vicinity of LANL.

From the LANL meeting, three laboratories and the Department of Energy, Office of International Health Programs (EH-63) agreed to participant and/or fund the study. The laboratories included: Los Alamos National Laboratory; Health and Ecological Assessment Division of the Lawrence Livermore National Laboratory and the University of Utah. The study was initiated in 2001 and completed in 2002. This document provides a summary of the results obtained for the mass spectrometric capabilities of the Los Alamos National Laboratory using thermal ionization mass spectrometry and the Lawrence Livermore National Laboratory using accelerator mass spectrometry.

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Experimental

The experimental design of the study was considered to be very realistic in terms of mimicking the typical isotopic ^{240}Pu to ^{239}Pu atom ratio for fallout, natural uranium interference level observed in background (non-exposed) populations and the ^{239}Pu excretion levels in urine by certain study groups. The intercomparison study involved the analysis of five replicates ^{239}Pu (plus ^{240}Pu at a constant ^{240}Pu: ^{239}Pu ratio and natural uranium) in synthetic urine samples at five concentration levels ranging from zero (blank samples) to ~56 μBq/sample. The laboratories were to analyze each sample according to their standard method protocol and report each measurement value along with its associated measurement uncertainty (propagated combined standard uncertainty).

Approach

In order to effectively minimize potential Pu contamination from chemical reagents and working environment, high purity reagents were used and the entire sample preparation was conducted in a Class-100 low-level radioactivity clean room facility at NIST.

Synthetic urine matrix

The synthetic urine sample blank material was prepared according to the recipe used in the first intercomparison study (Table 1) and by the Department of Energy in their DOE Laboratory Accreditation Program administered by the DOE Radiological and Environmental Sciences Laboratory. To minimize Pu contamination, ACS certified chemicals and distilled H2O were used for the sample matrix preparation.

Chemicals for making up the 216kg of synthetic urine were weighed accurately into separate clean PYREX beakers and completely dissolved in 1N HNO3 with gentle stirring and heating. Each of the resulting solutions was passed through a glass fiber filter (0.2 μm pore size) before transferring into a clean 225-liter polypropylene container. Following the addition of 22.2 g of l0mg/ml cesium carrier solution into the container, the mixture was diluted gravimetrically up to 216kg with 1N HNO3 made from concentrated HNO3 and distilled H2O. The synthetic urine matrix was then vigorously mixed and allowed to equilibrate at room temperature for 4 days. The matrix solution was inspected periodically and no precipitation was observed during the equilibrium period. The blank urine matrix solution was then pumped into 205 pre-cleaned and pre-weighed 1-liter size polypropylene bottles using a peristaltic pump. The filled bottles were weighed again to determine the mass of the matrix solution in each bottle. The prepared blank synthetic urine matrix had a density of 1.06g/ml and contained ~1 μ/g stable cesium and 1N HNO3.

Plutonium spiking solutions

The dilution and verification scheme for the preparation of the test samples appears in Fig. 1. The scheme was designed to prepare four test levels containing ^{239}Pu (plus ^{240}Pu at a constant ^{240}Pu: ^{239}Pu ratio and natural uranium at constant level) at approximately 3.6, 9, 29 and 56 μBq per one-liter sample. In addition, the blank synthetic urine samples contained uranium at a final concentration of 0.05 Bq/sample. The Pu spiking solutions were prepared from NIST primary standard reference materials, SRM-4330B (^{239}Pu) and SRM-4338A (^{240}Pu). The standard solution used for the U addition contained 5 Bq/ml of natural U and was prepared by diluting the NIST natural U (SRM-4321C) with 1N high purity HNO_3. The entire sample spiking and gravimetric dilution process for the individual synthetic urine samples was experimentally verified by alpha-spectrometry and gamma-spectrometry.[2] As shown in Fig. 1, Master-1 solution was prepared by gravimetric dilution of the ^{239}Pu and ^{240}Pu primary standards with 3N high purity HNO_3 containing 10 μ/g stable Cs. The amounts of the ^{239}Pu and ^{240}Pu added were managed to yield an atom ratio of ^{240}Pu/ ^{239}Pu to be ~0.15. The ^{134}Cs tracer was also added to the Master-1 solution at this step for the verification of the subsequent gravimetric dilutions. High acid concentration and stable Cs carrier were used to prevent Pu and ^{134}Cs from plating out of the solution.

Individual sample spiking

The prepared intercomparison samples were spiked individually with 0.06-0.15 g of the Master-L3 and -H3 solutions depending on the activity levels targeted. Within each test level, the spike additions were carefully controlled to minimize sample-to-sample activity variation. Following a careful mixing, the spiked samples were stored room temperature prior to the verification measurement.

Addition of natural uranium and mask of level signatures

Upon completion of the verification measurements, natural uranium and additional amounts of ^{134}Cs and ^{137}Cs tracers were added to each sample, including blank samples. The natural U content of each sample was elevated to ~0.05 Bq, a level typically found in the urine of non-affected populations in the vicinity of Los Alamos, NM. The standard solution used for U addition contained 5Bq/ml of natural U and was prepared by diluting the NIST natural lU (SRM-4321C) with IN high purity HN_3. About 10 μl of the diluted U standard solution was added to each urine sample using a micro volume pipettor. Tracing gravimetric dilutions with ^{134}Cs and ^{137}Cs resulted in each intercomparison sample bearing a distinctive Pu level-signature that can be revealed by gamma-counting of its ^{134}Cs or ^{137}Cs activities. Such level-signatures need to be erased prior to sample distribution. Similar to the method used for natural U addition, the level-signatures for the blank and the intercomparison samples were masked with appropriate amounts of ^{134}Cs and ^{137}Cs.

Dilution verification

To confirm gravimetric dilutions and ensure traceability of the intercomparison samples to the primary national standards, verification measurements were carried out in concert with the preparation

processes to establish the traceability link between the activities of ^{239}Pu and ^{240}Pu in the intercomparison samples and their primary standards. As shown in Fig. 1, two sets of check (CK) samples, 3 for each set, were taken at each step of the dilutions. The CK samples established an unbroken chain of comparison between the experimentally and the gravimetrically determined dilution factors. Two sets of CK samples were prepared to verify the dilution factors, DF1PU239 and DF1PU240 (from Pu SRMs to Master-1 solution), by alpha-spectrometry. The dilution factors, DFL2 and DFH2 (from Master-1 solution to Master-L2 and -H2 solutions) were determined by gamma-spectrometric analysis of ^{134}Cs. The same gamma-spectrometric analyses were performed for the determination of the dilution factors, DFL3 and DFH3 (from Master-L2 to Master-L3 and from Master-H2 to Master-H3). However, the ^{137}Cs added at the later stage of the dilutions was measured to verify the dilution factors of DFL3 and DFH3. All of the CK samples spiked with ^{134}Cs and ^{137}Cs were counted individually on a well-type NaI detector and their gross gamma-activities normalized to the added spiking solution were examined for consistency.

Analyte concentration uncertainties in test samples

Table 2 summarizes the relative uncertainty components and the estimated relative combined standard uncertainties of ^{239}Pu and ^{240}Pu activities in the prepared intercomparison samples. The relative combined standard uncertainties are derived as the root-sum-of-squares of the individual relative uncertainty components.

Analytical methods of participating laboratories using mass spectrometry

Table *3* summarizes the major analytical steps, test source preparation and instrument setup used by each laboratory to process the test samples. The reader is advised to directly contact the participating laboratories for additional chemical separations, test source mounting and measurement details.

Results

Outlier tests

Statistical analyses were performed on the reported data using Box and Whisker plots and Normal Probability plots to detect potential outlier results at the 95% confidence level. The Box and Whisker plots revealed more potential outliers compared to the Normal Probability plots. The results of the outlier tests revealed that LANL had no outliers for the ^{239}Pu results and two possible outliers (test levels 2 and 4) for the ^{240}Pu results. For LLNL, only one potential outlier in the second test level of the ^{239}Pu results and no potential outliers in the ^{240}Pu results were indicated. Although a very limited number of outliers were observed by the statistical tests, the outliers were not discounted or censored when calculating the mean bias, precision or detection limit parameters reported in this document.

Mean, standard deviation and bias

For each testing level, the mean and the standard deviation of the reported values, the difference between the laboratory's reported value and the NIST's value, and the mean difference (bias) from the NIST values were determined. For this study, the relative standard deviation of the five results per test level (including blanks) was used as an indicator for method precision. The percent relative standard deviation was expressed in terms of the percent of the mean test level value (coefficient of variation). In addition, for each test level data set, the standard deviation of the difference from the NIST value was calculated to determine precision as defined in the guidance provided in ANSI N13.30.[3] Tables 4 and 5 summarize the mean value and standard deviation of the five replicates for each test level as well as the mean difference from NIST for each ^{239}Pu test level in terms (μBq per sample. Table 6 provides the same summary for the ^{240}Pu sample results. The mean blank results were not subtracted from the submitted measurement values for the spiked testing ranges.

The information and data provided by each participant was used to estimated the typical combined standard uncertainty for a measurement for a given test level. Tables 7 summarize the ^{239}Pu and ^{240}Pu estimated combined standard uncertainties for each test level by participant.

Report of traceability for ^{239}Pu analyses

Tables 4 and 5 summarize each laboratory's mean bias for each test level, the determination of measurement traceability at each test level as the per ANSI N42.22[4] testing criterion and the determination of radiobioassay acceptable performance as per ANSI N13.30.
ANSI N42.22 defines the traceability limit to NIST for performance testing as:

$$|V_N - V_L| \leq 3\ \mathrm{SQRT}(\delta_N^2 + \delta_L^2)$$

where V_N is the NIST value, V_L is the laboratory value, δ_N is the combined standard uncertainty of V_N and δ_L is the combined standard uncertainty of V_L. For this study, the mean value and estimated combined standard uncertainty for each test level were used to evaluate conformance with the ANSI N42.22 performance criterion.

The acceptable ANSI 13.30 criteria for bias (average difference from the known testing value) and the standard deviation of the bias for a test level are 25 to +50%, and ±40% (1s), respectively.

Detection limits (MSAs)

The ^{239}Pu and ^{240}Pu data from each laboratory were statistically evaluated, in comparison to the NIST values, using a linear regression model. Figures 2 and 3 graphically illustrate the relationship of the LANL-TIMS and LLNL-AMS ^{239}Pu data with respect to the NIST values and the 90% prediction interval (two sided) for the fitted linear function. From this statistical analysis, an estimate of the decision level and detection limit for each mass spectrometric method was calculated based on the work of HUBAUX and Vos.[5] Table 8 summarizes the

detection limit estimate based on HUBAUX and Vos method as well as the classical method of CURRIE.[6] The estimated detection limits are based on a k_α and k_β=1.645.

Discussion

The observed performance of LANL and LLNL, as found in Tables 4 and 5 for ^{239}Pu and Table 6 for ^{240}Pu has been summarized below.

^{239}Pu method bias

When compared to the ANSI N13.30 testing criterion, both laboratories had an acceptable mean test level bias (difference from NIST) for the highest two testing levels (29 and 56 μBq/sample). It should be noted that, as a result of the measurement precision and the limited number of samples per test level, the calculated mean bias for both laboratories would not be statistically different from zero at the 5% significance level. Both the LLNL AMS and LANL TIMS had a calculated mean bias for the highest two test levels that was less than 5%, which indicates that their chemical yield monitors were accurately prepared and maintained with respect to their relationship to NIST standards.
For the lowest two test levels (3.6 and 8.9 μBq/sample), both LLNL AMS and LANL TIMS had a calculated negative mean bias between -8.2 and -12.8%. The reason for the "apparent" negative bias is not readily apparent since both labs had no significant biases (mean of blank value was not statistically different that zero at the 5% significance level) with respect to the measurement of the analytical blanks incorporated in the study.

^{240}Pu method bias

Table 6 summarizes the measured mean ^{240}Pu test level bias for both laboratories. Both laboratories had greater ^{240}Pu biases at all test levels compared to the ^{239}Pu biases measured at similar test levels. This was expected for these ^{240}Pu concentrations since the number of ^{240}Pu atoms was about seven times lower than the number of ^{239}Pu atoms in the test samples. The LLNL AMS method had the least bias for analyzing ^{240}Pu at all test levels. The measured bias for the LLNL measurement ranged from 0.69% to 14.6%, with the least bias being associated with the highest test level. For the LANL TIMS measurements, the mean bias per level varied from 11.7 at the highest test level to 83.1 at the lowest test level. A negative bias of -24.9% was noted for the 5.2 μBq/sample test level.

^{239}Pu precision

The calculated random uncertainty components (coefficient of variation of the five measurement with respect to the mean value) for each test level and laboratory have been summarized in Table 7 under the random and replicate column. For both LANL and LLNL, the calculated random uncertainty component per test level decreased with increasing ^{239}Pu concentration. This trend is consistent with expectations. Both LANL TIMS and LLNL AMS had excellent precision (<7%) at the two highest test levels. However, compared to LLNL AMS, the LANL TIMS method had a smaller coefficient of variation (1s) for the two highest testing levels (3.8% and 4.4%). However, at the two lowest test levels of 4 and 9 μBq/sample, LLNL's precision was found to be 31.3 and 11.4% (1s), respectively, or almost a factor of two better than LANL's precision at these test levels. At the lowest test level of 4 μBq, the method precision of LANL TIMS and LLNL AMS was consistent with expectations based on an estimated detection limit of 6 μBq/sample for both participants.

^{240}Pu precision

The mean ^{240}Pu precision values for each test levels, as measured by the coefficient of variation of the data per test level, have been summarized in Tables 6 and 7. Overall for the spiked test levels, the precision for the ^{240}Pu measurements was at least a factor of two more imprecise (and up to a factor of 8.2 more imprecise) than the precision for the ^{239}Pu measurements. LANL TIMS had the best ^{240}Pu precision for two highest test levels (16 and 32 μBq/sample) whereas LLNL AMS achieved better method precision for lowest test levels (2.1 and 5.2 (μBq/sample). Both the LLNL AMS and the LANL TIMS had similar coefficient of variation values for the blank analyses (~300 to 400%).

ANSI performance for ^{239}Pu measurements

The ^{239}Pu results from the laboratories were evaluated against ANSI N42.22 and ANSI N13.30 performance criteria (Tables 4 and 5). Both LANL and LLNL demonstrated their ability to make traceable measurements, per ANSI N42.22, at all four test levels. Both laboratories had sufficiently low biases at all test levels to meet the ANSI criterion for traceability.
Both laboratories passed the ANSI N13.30 performance criterion for ^{239}Pu bias (-25% to +50%) by a very substantial margin. In addition, LLNL passed the ANSI N13.30 precision criterion of ±40% for all test levels. LANL passed the precision criterion at all levels except the lowest test level of 3.57 μBq/sample. LANL's method precision at this test level was 55.5% or slightly greater than the required limit of ±40%.

Detection limits (MDAs)

Both laboratories had excellent detection capabilities for 239Pu in the synthetic urine samples. From this statistical analysis of the data, an estimate of the detection limit for each mass spectrometric method was calculated based on the work of HUBAUX and Vos5 and CURRIE6 (Table 8). The detection limit estimated by the HUBAUX and Vos approach uses the data for all test levels plus the blank results. Based on this approach, a detection limit of ~6 μBq/sample was estimated for both LANL and LLNL. Using the approach of CURRIE with blank data only, a detection limit of 0.82 and 5.2 (μBq/sample was estimated for LLNL and LANL, respectively. In the first intercomparison study, the estimated detection limit for LANL using an extrapolation and ANSI N13.30 approach was 0.6 μBq/200 g sample.

For ^{240}Pu, the estimated detection limit based on the HUBAUX and VOS approach was between 15-20 μBq/sample for both laboratories. LLNL had a much lower detection limit (2.1 μBq/sample) than LANL (24 (μBq/sample) when estimated using the currie approach.

Conclusions

This intercomparison study has shown that laboratories have developed state-of-the-art analytical methods for the determination of μBq levels of ^{239}Pu in urine specimens. However, this study is considered only a temporal snapshot of a laboratory's capability and does not reflect a laboratory's future capability or its routine operational performance for any given project or program. In general, based on the results of the first and second intercomparison studies that included four different methods, the performance in such studies may not be indicative of the method employed but the performance may be more reflective of the laboratory's proficiency, routine operational experience and the depth of technical experience for various study designs.

This second intercomparison study was somewhat different from the first study in terms of laboratory participants, study design and data assessment. Some of the data assessment methods used in the first study were retained in the second study. However, many new assessment tools were used in the second study that provided an alternative statistical approach for the measurement of outliers, bias, precision and quantification capability. As such, results of the two studies cannot be directly compared but certain inferences can be made. The approach to estimate and compare method detection capabilities (MDA) were quite different and, as a result, the stated method detection values estimated in the first study may be, for some laboratories, lower than those estimated in this study. It is believed that these study design and data assessment enhancements of the second study provided a more realistic study and laboratory performance evaluations.

The performance of both the LANL TIMS and LLNL AMS, in terms of ^{239}Pu bias and precision, was in compliance with the ANSI N13.30 performance requirements for all test levels except for LANL at the lowest test level. For the two test levels above 29 μBq/sample, the measured bias (as per ANSI N13.30) for both laboratories was less than 5%. The most severe bias for ^{239}Pu, of only ~13%, was noted for the 9 μBq/sample test level. The measured ^{240}Pu bias varied from <1% at the highest test level (32 μBq/sample) to 83% at the lowest test level (2.1 μBq/sample). For both laboratories, the measured method precision for either plutonium isotope decreased with increasing test level concentration, with the best ^{239}Pu precision (3.8%) noted for LANL at the highest test level (29 μBq/sample). The excellent ^{239}Pu precision indicates that both laboratories had a good blank control process and a knowledge of the parameters contributing to the uncertainty of the method. For both laboratories, the ^{240}Pu precision for all test levels was at least a factor 2 worse, but up to 8 times worse, than the measured ^{239}Pu precision. The LLNL AMS method performed at least as well as the LANL TIMS method in terms of precision for both plutonium isotopes, and for accuracy (bias) for ^{239}Pu. The AMS method was found to have a smaller ^{240}Pu bias when compared to the TIMS method.

For both laboratories, the detection capability (MDA) based on a regression method was estimated to be 5 to 6 (μBq/sample for ^{239}Pu and ~20 μBq/sample for ^{240}Pu. In comparison to the regression method to estimate the MDA values, LLNL had much lower MDA values for both isotopes using the Currie method to estimate the MDAs. These detection limits appear to be the best that can be attained for ^{239}Pu and ^{239}Pu radiobioassay urine measurements. The LANL TIMS ^{239}Pu MDA of 5 to 6 μBq estimated for this study was about an order of magnitude greater than that estimated for the first study. However, the estimated ^{239}Pu MDA in the first study was estimated by a different statistical analysis.

For detectable concentrations, the performance (accuracy and precision) of mass spectrometric methods for the radiobioassay of urine samples is excellent and equivalent to radioanalytical method using radioactive decay emission analysis (alpha-spectrometry). However, the detection capability of the mass spectrometric methods is several orders of magnitude better than that of alpha-spectrometry.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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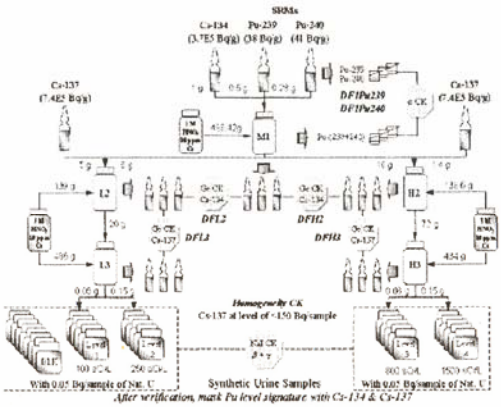

Fig. 1. Dilution and verification scheme

CH_4N_2O	Urea	98	16
HNO_3	Nitric acid	70	70.67
H_2O	Distilled water	100	950

Table 2. The uncertainty components and derived combined standard uncertainty of ^{239}Pu and ^{240}Pu activities in the samples

Sample activity	Source of relative uncertainty component, %			
	SRM	Gravimetric measurement and buoyance correction	Decay correction	Relative combined standard uncertainty, %
For ^{239}Pu:				
Levels 1 & 2	0.68	0.28	–	0.74
Levels 3 & 4	0.68	0.34	–	0.76
For ^{240}Pu:				
Levels 1 & 2	0.76	0.28	0.17	0.83
Levels 3 & 4	0.76	0.34	0.17	0.85

The uncertainties listed are the relative expended uncertainties with a coverage factor of $k = 2$.
For ^{239}Pu, the Level-1, -2, -3, and -4 represent activities at ~4, 9, 29, and 56 μBq/sample, respectively.
For ^{240}Pu, the Level-1, -2, -3, and -4 represent activities at ~1.7, 5, 16, and 31 μBq/sample, respectively.

Table 3. Summary of radiochemical and instrumental methods used by the participating laboratories

	LANL – TIMS	LLNL – AMS
Sample preparation	Calcium phosphate co-precipitate, dissolved in 8M HNO_3	Calcium phosphate, co-precipitated from HNO_3 – H_2O_2 solution, dissolved in 8M HNO_3, sodium nitrite to adjust Pu to Pu(IV)
Yield monitor	^{242}Pu	^{242}Pu
Chemical separations	AG1X4, 8M HNO_3 wash, 0.36N HCl plus HI-HCl elute, electrodeposit from Na_2SO_4 solution, alpha count; strip from plate with HF and HNO_3, AG MP-1, 8M HNO_3, 0.5 HCl/HI-HCl (1:9 vol.) elute, AG MP-1, H_2O_2 – HCl load, H_2O_2 – HCl/8M HNO_3 washes, HBr elution, conc. HNO_3 & $HClO_4$ treatment	AG1X8, 10 column volumes of 8M HNO_3/10M HCl washes, NH_4I-HCl elute, co-precipitated with Fe hydroxide
Source preparation	Pu electrodeposited onto rhenium (Re) filament with platinum DNS* from NH_4Cl-HCl solution	Nb added to $Fe(OH)_3$ precipitate and heated to 800 °C. Dried precipitate packed into cathode
Instrumental method	Single stage ion-counting thermal ionization mass spectrometry, 60 minute analysis	Accelerator mass-spectrometry

*Dinitrito sulfato platinus acid..

Table 4. Evaluation of LANL's TIMS ^{239}Pu results

Test level, µBq/sample	NIST values		LANL value		Difference, %	ANSI N42.22 traceable	ANSI N42.22 limit	ANSI N13.30 criteria (pass/fail)	
	µBq/sample	CSU* 2s %	µBq/sample	Std. dev. of test level samples 2s %				Bias (–25% to +50%)	Precision – std. dev. of bias (±40% 1s)
4	3.57	1.58	3.15	111	–11.8	Yes	147	Pass	Fail
9	9.08	0.89	7.92	65.4	–12.8	Yes	86	Pass	Pass
29	28.7	0.98	29.5	7.50	2.79	Yes	12	Pass	Pass
56	55.6	0.89	58.0	8.80	4.32	Yes	14	Pass	Pass
Blank	0	NA	–0.854	322	NA	NA	NA	NA	NA

* Combined standard uncertainty.

Table 5. Evaluation of LLNL's AMS ^{239}Pu results

Test level µBq/sample	NIST values		LLNL value		Difference, %	ANSI N42.22 traceable	ANSI N42.22 limit	ANSI N13.30 criteria (pass/ fail)	
	µBq/sample	CSU 2s %	µBq/sample	Std. dev. of test level samples 2s %				Bias (–25% to +50%)	Precision – std. dev. of bias (±40%)
4	3.67	1.08	3.37	62.6	–8.17	Yes	86	Pass	Pass
9	9.23	0.93	8.09	22.8	–12.4	Yes	30	Pass	Pass
29	28.9	1.23	28.5	14.6	–1.38	Yes	22	Pass	Pass
56	56.3	0.91	55.5	15.0	–1.42	Yes	22	Pass	Pass
Blank	0	NA	0.157	274	NA	NA	NA	NA	NA

* Combined standard uncertainty.

Table 6. Evaluation of LANL's TIMS and LLNL's AMS ^{240}Pu results

Test level µBq/sample	NIST		LANL TIMS			LLNL AMS		
	Mean µBq/sample LANL/LLNL	1s %	Mean, µBq/sample	1s %	Diff. from NIST, %	Mean, µBq/sample	1s %	Diff. from NIST, %
2.1	2.02/2.07	0.69/0.39	3.67	190	83.1	2.01	82.3	–2.86
5.2	5.13/5.21	0.25/0.29	3.86	126	–24.9	4.45	89.9	–14.6
16	16.2/16.3	0.31/0.49	22.2	21.2	36.9	16.0	26.8	–2.00
32	31.4/31.8	0.22/0.25	35.1	11.9	11.7	31.6	27.1	–0.69

Table 7. Summary of standard uncertainty components for ^{239}Pu by participant

Level or participant	Relative standard uncertainty component, % 1s					Combined standard uncertainty,* % 1s	
	Replicate and random*		Tracer	Gravimetric or volumetric	Blank correction	^{239}Pu	^{240}Pu
	^{239}Pu	^{240}Pu					
Blank							
LANL-TIMS	161	289.7		0.28	100.5	57.0	102
LLNL-AMS	137	436	3.3	0.25	66.7	48.4	154
Level-1							
LANL-TIMS	55.5	189.7	0.32	0.28	100.5	24.9	84.9
LLNL-AMS	31.1	82.3	3.3	0.25	66.7	14.3	36.9
Level-2							
LANL-TIMS	32.7	126.1	0.32	0.28	100.5	14.7	56.4
LLNL-AMS	10.9	89.9	3.3	0.25	66.7	5.9	40.3
Level-3							
LANL-TIMS	3.75	21.2	0.32	0.28	100.5	2.6	9.5
LLNL-AMS	6.48	26.8	3.3	0.25	66.7	4.4	12.4
Level-4							
LANL-TIMS	4.38	11.9	0.32	0.28	100.5	2.8	5.3
LLNL-AMS	6.73	27.1	3.3	0.25	66.7	4.5	12.5

The combined standard uncertainty (CSU) is a quadratic sum of the identified standard uncertainty components, except the component of blank correction. Even though the standard uncertainty on blank value is large, the uncertainty from blank correction is normally insignificant as a result of its small sensitivity factor defined in error propagation function.

* The standard error of the random component was combined into the CSU. For ^{239}Pu, the Level-1, -2, -3, and -4 represent activities at 4, 9, 29, and 56 μBq/sample, respectively. For ^{240}Pu, the Level-1, -2, -3, and -4 represent activities at 1.7, 5, 16, and 31 μBq/sample, respectively.

Table 8. Estimate of the detection limit from the data reported

Participant	Detection limit estimate, Bq/sample			
	^{239}Pu CURRIE[6]	^{239}Pu regression[5]	^{240}Pu CURRIE[6]	^{240}Pu regression[5]
LANL TIMS	5.2	6.3	24	20
LLNL AMS	0.82	6.1	2.1	15

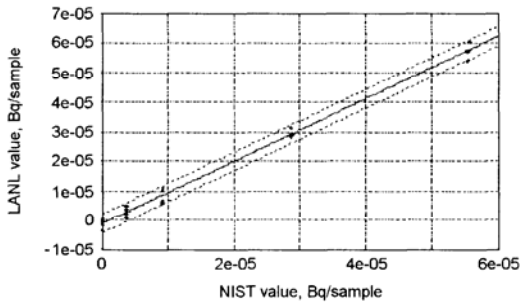

Fig. 2. LANL TIMS ^{239}Pu results compared to NIST values. Regression analysis: $y = a+bx$; $a = -9.92e{-}07$; $b = 1.06$; 90% prediction interval

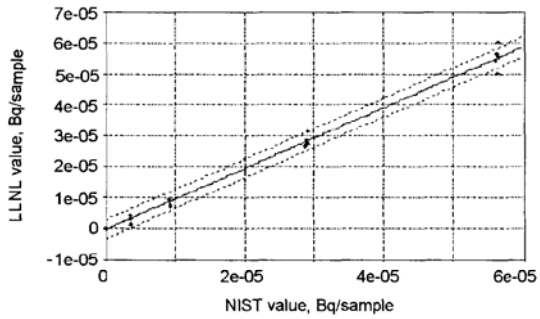

Fig. 3. LLNL AMS ^{239}Pu results compared to NIST values. Regression analysis: $y = a+bx$; $a = -2.43e{-}07$; $b = 0.989$; 90% prediction interval